

Decomposition of Acyl Peroxides in Acid
Medium

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B001/B066

possible. Apart from the papers of Refs. 6 - 8, no papers have been published so far on the reaction products of benzoyl and acetyl-benzoyl peroxide in benzoic acid, and of m-nitro-benzoyl peroxide in acetic acid. The authors therefore first determined the principal products of these reactions. They studied the decomposition of benzoyl-, acetyl-benzoyl- and m-nitro-benzoyl peroxides in acetic and benzoic acid labeled with C^{14} in the carboxyl. The separating carbon dioxide gas was found to contain 2 - 25 % of radioactive $C^{14}O_2$. Decomposition of benzoyl- and m-nitro-benzoyl peroxide in deuterated acetic acid (CH_3COOD) disclosed that the R-radical of the peroxide splits off 1 - 3 % deuterium from the carboxyl group of the acid ($R = C_6H_5, C_6H_4NO_2$). The separation of the labeled $C^{14}O_2$ is explained by the "relay-transfer" of the acyloxy radicals in carboxylic acid medium. The only possible source of the $C^{14}O_2$ formation is thus the decarboxylation of the $RC^{14}OO\cdot$ radicals of the labeled solvent. Contrary to the remaining peroxides, acetyl benzoyl peroxide gives a considerable quantity of methyl benzoate on decomposition into acids,

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especially in the case of benzoic acid (70 %), which may be explained by the reaction $C_6H_5COOOCOCH_3 \longrightarrow C_6H_5COOCH_3 + CO_2$ (2). Table 2 summarizes the experimental results on the decomposition of benzoyl-m-nitro-benzoyl peroxide dissolved in CH_3COOD ; they show that in the case of the phenyl radical, the deuterium separation is 3 %, and in the case of the nitro-phenyl radical 1.2 %. With m-nitro-benzoyl peroxide the ratio of $C_6H_4DNO_2 : C^{14}O_2$ is only 1 %. S. F. Zhil'tsov is thanked for carrying out the radiometric determinations. There are 2 tables and 11 references: 5 Soviet, 4 US, and 2 British.

ASSOCIATION: Nauchno-issledovatel'skiy institut khimii pri Gor'kovskom gosudarstvennom universitete (Scientific Research Institute of Chemistry at the Gor'kiy State University)

SUBMITTED: January 29, 1960

Card 3/3

88489

S/079/61/031/001/024/025
B001/B066

5.3200 2209

AUTHORS: Razuvayev, G. A., Likhterov, V. R., and Etlis, V. S.

TITLE: Study of the Thermal Decomposition of Acetyl-cyclohexane-sulfonyl Peroxide in Different Solvents

PERIODICAL: Zhurnal obshchey khimii, 1961, Vol. 31, No. 1, pp. 274 - 280

TEXT: The authors studied some reactions of acetyl-cyclohexane-sulfonyl peroxide which gives two different radicals in the homolytic decomposition, i. e. cyclo-C₆H₁₁SO₂O[•] and CH₃COO[•]. Their properties could be compared and some new data on the reaction mechanism of acyl peroxides could be obtained in this way. Organic solvents with different capability of giving off their hydrogen atoms to free peroxide radicals, and saturated halogen-containing solvents were selected for this thermal peroxide decomposition. Kinetic studies were performed in isopropyl alcohol, cyclohexane, benzene, and carbon tetrachloride. The decomposition reaction was found to obey the kinetic law of first order (Diagrams 1 - 4) (Ref. 5). The activation energies in the corresponding solvents were calculated from the slope of

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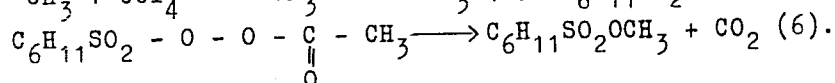
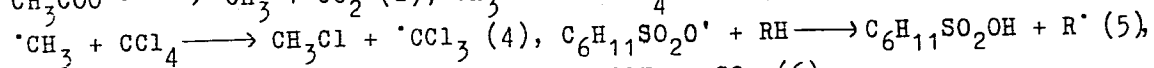
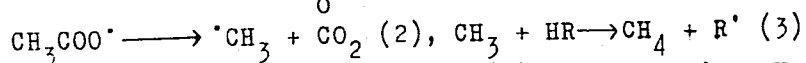
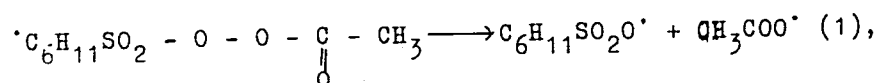
the straight line (Diagram 5). They were (kcal/mole) in $i\text{-C}_3\text{H}_7\text{OH}$: 25.5;
in cyclo- C_6H_{12} : 23.4; in C_6H_6 : 25.6; in CCl_3 : 26.8. The results indicate
that the decomposition rate of acetyl-cyclohexane-sulfonyl peroxide de-
creases in the following order, depending on the solvents used: isopropyl
alcohol > cyclohexane > benzene > CCl_4 . It must be noted that the values of
the activation energies of these solvents differ little from one another.
On reaction of the peroxide with the above solvents the following com-
pounds were obtained: cyclohexane- and cyclohexene sulfonic acids, acetic
acid, methane, methyl chloride, CO_2 , methyl- and cyclohexyl esters of
cyclohexane sulfonic acid, hexachloro ethane, acetone, cyclohexene. The
kinetic studies of the thermal decomposition of acetyl-cyclohexane-sulfonyl
peroxide, as well as the data of analysis and identification of the
separated products suggest two reaction routes, a) a free-radical
mechanism and b) a molecular reaction. Ad a) equations (1) - (5), ad
b) equation (6):

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Study of the Thermal Decomposition of Acetyl-
cyclohexane-sulfonyl Peroxide in Different
Solvents

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Yu. A. Kaplin is thanked for his co-operation. There are 5 figures,
5 tables, and 12 references: 6 Soviet, 3 US, 2 German, and 1 Soviet patent.

SUBMITTED: January 8, 1960

X

Card 3/3

RAZUVAYEV, G.A.; DERGUNOV, Yu.I.; VYAZANKIN, N.S.

Reaction of tetraethyllead with halogenated hydrocarbons. Zhur.
ob. khim. 31 no.3:998-1003 Mr '61. (MIRA 14:3)

1. Nauchno-issledovatel'skiy institut khimii pri Gor'kovskom
gosudarstvennom universitete imeni N. I. Lobachevskogo.
(Lead) (Hydrocarbons)

RAZUVAYEV, G.A.; LATYAYEVA, V.N., kand.khim.nauk; BRILKINA, T.G., kand.khim.
nauk.

Homolytic reactions in the liquid phase. Vest. AN SSSR 31
no.4:124-127 Ap '61. (MIRA 14:4)

1. Chlen-korrespondent AN SSSR (for Razuvayev).
(Chemical reactions)

RAZUVAYEV, G.A.; ETLIS, V.S.; GROBOV, L.N.

Interaction between sulfurous anhydride and certain alkylene
oxides. Zhur. ob. khim. 31 no.4:1328-1332 Ap '61. (MIRA 14:4)
(Sulfur dioxide)
(Olefins)

RAZUVAYEV, G.A.; ETLIS, V.S.; GROBOV, L.N.

Degradation of some low molecular weight polysulfites. Zhur.
ob. khim. 31 no.4:1332-1334 Ap '61. (MIRA 14:4)
(Sulfites)

20952

S/079/61/031/004/006/006
B118/B208

15 8114 2209, 1372, 1407

AUTHORS: Razuvayev, G.A., Shchepetkova, O.A., and Vyazankin, N.S.

TITLE: Structure of some organo-tin polymers

PERIODICAL: Zhurnal obshchey khimii, v. 31, no. 4, 1961, 1401

TEXT: It was previously found (Ref. 2: ZhOKh., 30, 2498 (1960)) that benzoyl peroxide cleft the Sn bond in hexaethyl distannane even under mild conditions:

$(C_6H_5COO)_2 + (C_2H_5)_3Sn-Sn(C_2H_5)_3 \longrightarrow 2(C_2H_5)_3SnOCOC_6H_5$. This reaction could

be applied to the structural analysis of organo-tin compounds. This reaction takes place even at room temperature without separation of CO_2 and

gaseous hydrocarbons. This indicates the absence of side reactions, so that only the Sn-Sn bond in the polymer, and the C-O bond in the peroxide are cleft. The authors of the present paper isolated the benzoate of triethyl tin (I) and the dibenzoate of diethyl tin (II) (melting point

122-123°C) by reacting the peroxide with the polymer. Besides, metallic

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S/079/61/031/004/006/006
B118/B208

Structure of some organo-tin ...

tin and the tribenzoate of ethyl tin (III) (melting point 185-188°C under decomposition) were separated. If the polymer were of the linear type $(C_2H_5)_3Sn-[Sn(C_2H_5)_2]_n-Sn(C_2H_5)_3$, only the formation of compounds (I) (from primary tin atoms) and (II) (from secondary tin atoms) would have to be expected, provided that no disproportionation of compound (II) to (I) and (III) takes place. It was found from the quantitative ratio of the reaction products that 23.6 % of the tin atoms have primary, 19.9 % secondary, and 27.6 % tertiary character. 28.8 % of the metal atoms in the polymer mass were in the elementary state. It is possible that metallic tin is formed from quaternary atoms. The results obtained correspond to earlier concepts on the branching of chains in intermediates of disproportionations of hexaethyl distannane (Ref. 1: DAN SSSR, 132, 364 (1960)), and of hexaethyl diplumbane (Ref. 3: ZhOKh, 30, 1310 (1960)). There are 3 Soviet-bloc references.

ASSOCIATION: Nauchno-issledovatel'skiy institut khimii pri Gor'kovskom gosudarstvennom universitete imeni N.I. Lobachevskogo
(Scientific Research Institute of Chemistry Gor'kiy State University imeni N.I. Lobachevskiy)

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20752

Structure of some organo-tin ...

S/079/61/031/004/006/006
B118/B208

SUBMITTED: November 4, 1960

Card 3/3

RAZUZAYEV, G.A.; VYAZANKIN, N.S.; DERGUNOV, Yu.I.; VYSHINSKIY, N.N.

Thermal decomposition of tetraethyllead, hexaethylplumbane, and their analogs. Part 5: Reactions of decomposition and disproportionation of hexaethyldistannane. Zhur.ob.khim. 31 no.5:1712-1717 My '61. (MIRA 14:5)

1. Nauchno-issledovatel'skiy institut khimii pri Gor'kovskom gosudarstvennom universitete imeni N.I.Lobachevskogo.
(Tin organic compounds)

RAZUVAYEV, G.A.; MITROFANOVA, Ye.V.; PETUKHOV, G.G.

Reactions of triethylaluminum and triphenylaluminum with
benzoyl peroxide in benzene solution. Zhur.ob.khim. 31 no.7:
2340-2343 J1 '61. (MIRA 14:7)

1. Gor'kovskiy gosudarstvennyy universitet.
(Aluminum) (Benzoyl peroxide)

RAZUVAYEV, G.A.; MITROFANOVA, Ye.V.; PETUKHOV, G.G.

Oxidation of triphenylaluminum and phenyllithium. Zhur.ob.khim.
31 no.7:2343-2347 J1 '61. (MIRA 14:7)
(Aluminum) (Lithium) (Oxidation)

RAZUVAYEV, G.A.; PETUKHOV, G.G.; GALIULINA, R.F.; BREVNOVA, T.N.

Investigating the reactivity of phenyllithium by means of
exchange reactions. Zhur.ob.khim. 31 no.7:2347-2349 J1 '61.
(MIRA 14:7)

(Lithium) (Benzene)

RAZUVAYEV, G.A.; PETUKHOV, G.G.; OSANOVA, N.A.

Investigating the reaction of pentaphenyl phosphorus with
benzene by means of tagged atoms. Zhur.ob.khim. 31 no.7:
2350-2353 Ji '61. (MIRA 14:7)
(Phosphorus organic compounds) (Benzene)

5 3700

25368
S/079/61/031/008/006/009
D215/D304

AUTHORS: Razuvyev, G.A., Latayeva, V.N. and Vyshinskaya, L.I.
TITLE: Free radicals reactions of biscyclopentadiene-diphenyl titanium
PERIODICAL: Zhurnal obshchey khimii, v. 31, no. 8, 1961, 2667-2674

TEXT: The authors give a short survey of achievements in the field of organic titanium compounds and their brief characteristics, all based exclusively on western publications. In their experimental work they investigated the behaviour of $(C_5H_5)_2Ti(C_5H_5)_2$ under reaction conditions, used previously for phenyl derivatives of other metals. They investigated the reactions of this compound with different solvents: benzene, methyl and isopropyl alcohols, $CHCl_3$ and CCl_4 . When the solutions of the compound were heated in sealed tubes in complete absence of oxygen, a sharp change in their color was observed, from the

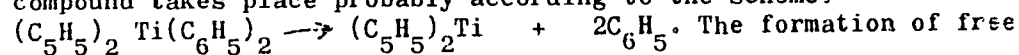
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D215/D304

Free radicals...

initial yellow one to a dark green, which is the color of titanium compounds of lower valencies. The reduction of the titano-organic compound takes place probably according to the scheme:



phenyl radicals was confirmed by the authors' further experiments: the free radicals removed hydrogen from alcohols and CHCl_3 , chlorine

from CCl_4 , dimerized in benzene and reacted with metallic Mg in a CCl_4

solution. $(\text{C}_5\text{H}_5)_2\text{Ti}(\text{C}_6\text{H}_5)_2$ is fairly stable in benzene or alcohol solutions, but is easily converted to the dichloride in CCl_4 alone, or in

the presence of mercuric chloride, in which case the phenyl group is exchanged for the chloro group and $(\text{C}_5\text{H}_5)_2\text{TiCl}_2$ and $\text{C}_6\text{H}_5\text{MgCl}$ are obtained.

This exchange reaction (yield \pm 70%) takes place simultaneously with that of free radicals. The reverse reaction of replacement of chloro by the phenyl group takes place when the dichloride is heated with phenylmercuric

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S/079/61/031/008/006/009
D215/D304

Free radicals...

chloride. There are 1 graph and 16 references: 2 Soviet-bloc and 14 non-Soviet-bloc. The references to the 4 most recent English-language publications read as follows: C.H.E. Bawn, I. Gladstone, Pr. Chem. Soc. 227, (1959); A. Jensen, F. Basals, J. Am. Chem. Soc. 81, 3813, (1959); W.P. Long, J. Am. Chem. Soc. 81, 5312, (1959); and D. H. Hey, T. Peters, J. Chem. Soc. 79, (1960).

SUBMITTED: July 14, 1960

Card 3/3

TERMAN, L.M.; RAZUVAYEV, G.A.

Radical reactions of peroxyarbonates. Part 2: Decomposition of dicyclohexylperoxydicarbonate in benzene and acetic acid in the presence of metals and metal salts. Zhur.ob.khim. 31 no.9:3132-3136 S '61. (MIRA 14:9)

(Peroxyarbonates) (Radicals (Chemistry))

RAZUVAYEV, G.A.; BOGUSLAVSKAYA, L.S.

Synthesis by means of free hydroxyl radicals. Part 2: Reactions
of aliphatic esters with hydroxyl radicals. Zhur.ob.khim. 31
no.10:3440-3447, 0 '61. (MIRA 14:10)
(Esters) (Hydroxyl group)

RAZUVAYEV, G.A.; VYAZANKIN, N.S.; SHCHEPETKOVA, O.A.

Mechanism of the reaction of hexaethyldistannane disproportionation.
Zhur. ob. khim. 31 no. 11:3762-3768 N '61. (MIRA 14:11)

1. Nauchno-issledovatel'skiy institut khimii pri Gor'kovskom
gosudarstvennom universitete imeni N.I. Lobachevskogo.
(Tin compounds)

RAZUVAYEV, G.A.

5 3700

31196
S/079/61/031/012/010/011
D204/D301

AUTHORS: Razuvayev, G. A., Vyazankin, N. S., D'yachkovskaya, O.S., Kiseleva, I. G., and Dergunov, Yu. I.

TITLE: Certain reactions of the organometallic compounds of Group IV elements, catalyzed by aluminum chloride

PERIODICAL: Zhurnal obshchey khimii, v. 31, no. 12, 1961, 4056

TEXT: A continuation of previous work, in which it has been shown that $(Et)_3SiCl$ and $(Et)_3SnCl$ could be obtained in high yields by the action of $iso-C_3H_7Cl$ on $(Et)_4Si$ and $(Et)_4Sn$ in presence of $AlCl_3$. This reaction has been used in the present work to synthesize $(Et)_5Si_2Br$ and compounds $(Et)_3MX$, where $M = Si, Ge, Sn$ and $X = Cl, Br$, in 60-90% yields. These were prepared by the dropwise addition of equimolar quantities of $iso-C_3H_7X$ to $(Et)_4M$ containing ~2% $AlCl_3$ and heating until the gaseous products were evolved (~4

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Certain reactions of the ...

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D204/D301

hours). $(Et)_5Si_2Br$ was converted to decaethyl tetrasilane (b.p. 164-170°C/1 mm Hg, $n_D^{20} = 1.5160$) by the action of highly dispersed fused Na, in 20.2% yield. It was also established that compounds of type $(Et)_6M_2$, where $M = Si, S$, disproportionate to $(Et)_4M$ and M, on heating to 235°C in the presence of 3 - 5% $AlCl_3$. There are 1 table and 2 references: 1 Soviet-bloc and 1 non-Soviet-bloc. The reference to the English-language publication reads as follows: H. Gilman, R. K. Ingham and A. G. Smith, J. Org. Ch., 18, 1743, (1953).

ASSOCIATION: Nauchno-issledovatel'skiy institut khimii pri Gor'-kovskom gosudarstvennom universitete imeni N. I. Lobacheskogo (Scientific Research Institute of Chemistry, Gor'kiy State University im. N. I. Lobacheskii)

SUBMITTED: July 3, 1961

Card 2/2

RAZUVAYEV, G.A.; VASILEYSKAYA, N.S.; BYCHKOV, V.T.; MAKAR'YEVA, A.Ye.

Photoreaction of carbon tetrachloride with dioxane. Zhur.ob.khim.
31 no.12:4057-4058 D '61. (MIRA 15:2)

(Carbon tetrachloride)
(Dioxane)

RAZUVAYEV, G.A.; TERMAN, L.M.; PETUNHOV, G.G.

Mechanism of the thermal degradation of percarbonates in solution.
Dokl. AN SSSR 136 no.3:628-630 Ja '61. (MIRA 14:2)

1. Chlen-korrespondent AN SSSR (for Razuvayev).
(Peroxyarbonates)

TERMAN, L.M.; RAZUVAYEV, G.A.; PETUKHOV, G.G.

Addition of isopropyl alcohol to maleic acid, initiated by
percarbonates. Dokl. AN SSSR 136 no.6:1349-1350 F '61.

(MIRA 14:3)

1. Chlen-korrespondent AN SSSR (for Razuvayev).
(Isopropyl alcohol)
(Maleic acid)
(Peroxy carbonates)

21570

S/020/61/137/003/022/030
B103/B208

5.3700 1209

AUTHORS: Razuvayev, G. A., Corresponding Member AS USSR,
D'yachkovskaya, O. S., Vyazankin, N. S., and Shchepetkova,
O. A.

TITLE: Reactions of acyl peroxides with organic derivatives of
lead, tin, and silicon

PERIODICAL: Doklady Akademii nauk SSSR, v. 137, no. 3, 1961, 618-621

TEXT: The authors discuss and compare the reactions of benzoyl peroxide (BP) and acetylbenzoyl peroxide (ABP) with organic derivatives of tin, lead, and silicon without solvent and under exclusion of atmospheric oxygen. They believe that the σ -bond may be ruptured at the same time according to two mechanisms in the case of the organotin compound:
1) via formation of an active complex, 2) via formation of kinetically independent particles. In this way, the number of end products increases. As the reactions discussed (Table 1) take place only at elevated temperatures, the authors assume that these reactions may be due to decomposition of peroxides: $C_6H_5COOOCOR \rightarrow C_6H_5COO\cdot + RCOO\cdot$ (1), where $R = C_6H_5$ or CH_3 ;

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Reactions of acyl peroxides ...

$C_6H_5COO\cdot \rightarrow C_6H_5\cdot + CO_2$ (2). The latter, however, is of minor importance. The resultant free benzoyloxy radicals react with organotin compounds, with substitution of benzoate radicals for the ethyl radicals in the latter: $C_6H_5COO\cdot + (C_2H_5)_3SnX \rightarrow (C_2H_5)_2SnX(OCOC_6H_5) + C_2H_5\cdot$ (3). Here and henceforward, $X = C_2H_5, Cl, Br, C_6H_5COO$. The results of experiments 1-4 indicate that the nature of X affects the course of (3) only little. In the case $X = Cl$ and Br , the authors isolated only diethyl tin dibenzoate and diethyl tin dihalide, apparently owing to disproportionation: $2(C_2H_5)_2SnX(OCOC_6H_5) \rightarrow (C_2H_5)_2SnX_2 + (C_2H_5)Sn(OCOC_6H_5)_2$ (4). The free ethyl radicals resulting in (3) disproportionate and are slightly dimerized: $2C_2H_5\cdot \rightarrow C_2H_6 + C_2H_4$ (5); $2C_2H_5\cdot \rightarrow n-C_4H_{10}$ (6). The low total amount of gaseous hydrocarbons (less than 1 mole per mole of decomposed peroxide; experiments 1-4) suggests that the ethyl radicals initiate PB decomposition and give ethyl benzoate (experiment 4). In this way, the authors explain the formation of all products confirmed on the basis of a scheme of free-radical interaction. As, however,

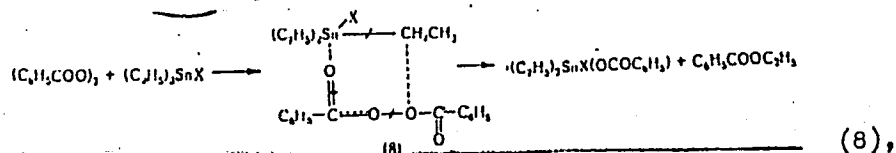
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21570

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B103/B208

Reactions of acyl peroxides ...

ethylbenzoate may likewise be formed by a reaction with the active complex



the authors studied the interaction of ABP with tetraethyl tin and triethyl tin chloride (experiments 5 and 6). They conclude from the resultant reaction products that in this case the afore-mentioned modes (1 and 2) of homolytic rupture of the covalent bond occurred. The reaction of BP with tetraethyl lead (experiment 7) does not essentially differ from the one discussed above. Here, (2) is almost insignificant. The reaction of acyl peroxides with tetraethyl silane (experiments 8 and 9) proceeds quite differently; here, processes of the kind of (3) and (8) are missing, the Si-C bond being obviously stable to homolytic rupture. The initial stage of these reactions is assumed to be based upon decomposition of acyl peroxides according to (1), (2), and $\text{CH}_3\text{COO} \cdot \longrightarrow \text{CH}_3 \cdot + \text{CO}_2$ (9).

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B103/B208

Reactions of acyl peroxides ...

The resultant free radicals remove the hydrogen from the tetraethyl silane molecules to give benzoic acid, benzene, and methane. Complex organosilicon compounds with two or more silicon atoms in the molecule are formed by recombination of the secondary radicals. They will be later described. $C_{16}H_{38}Si_2$ is given as an example. The reactions of similar organotin and organosilicon compounds with peroxides being considerably different, the authors studied the interaction of BP with the organotin analog of trimethyl-phenyl silane (experiment 10). No gaseous hydrocarbons were formed in this case and CO_2 yield was low. The authors conclude from this that (2) is only a side reaction, and that no CH_3 radicals are displaced by benzoate radicals in this case. Trimethyl tin benzoate, on the other hand, is obtained in a high yield: $(CH_3)_3SnOH + C_6H_5COOH \rightarrow (CH_3)_3SnOCOC_6H_5 + H_2O$ (10). This indicates that the σ bond between the benzene ring and the metal atom in the trimethyl-phenyl tin molecule is most strongly subjected to homolytic cleavage. Since only 0.1 mole of diphenyl per mole of decomposed peroxide is formed, no analogy with the interactions between BP and trimethyl silane has been

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Reactions of acyl peroxides ...

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established. In the reaction of BP with triethyl silane (experiment 11), mainly the Si-H bond is cleft, giving triethyl silicon benzoate as the most important silicon-containing product. In this case, apparently also processes take place which remind of (3), since small quantities of ethane, ethylene, and butane result. The authors continue their studies. There are 1 table and 3 references: 1 Soviet-bloc and 2 non-Soviet-bloc. The reference to the English-language publication reads as follows: Ref. 1, L. Jaffe, E. J. Prosen, M. Szwarc, J. Chem. Phys., 27, 416 (1957).

ASSOCIATION: Nauchno-issledovatel'skiy institut khimii pri Gor'kovskom gosudarstvennom universitete im. N. I. Lobachevskogo (Scientific Research Institute of Chemistry, Gor'kiy State University imeni N. I. Lobachevskiy)

SUBMITTED: November 9, 1960

Card 5/8

RABINOVICH, I.B.; TEL'NOY, V.I.; NIKOLAYEV, P.N.; RAZUVAYEV, G.A.; Prinimala uchastiye: KIRILLOVA, A.S.

Thermochemistry of the interaction between hexaethyldistannane and benzoyl peroxide. Dokl.AN SSSR 138 no.4:852-855 Je '61.
(MIRA 14:5)

1. Institut khimii pri Gor'kovskom gosudarstvennom universitete imeni N.I.Lobachevskogo. 2. Chlen-korrespondent AN SSSR (for Razuvayev).
(Tin compounds) (Benzoyl peroxide)

5.3700

25319

S/020/61/138/005/019/025
B103/B220

AUTHORS: Razuvaev, G. A., Corresponding Member AS USSR, Latyaeva, V.N.,
and Vyshinskaya, L. I.

TITLE: Reaction of benzoyl peroxide with titanocene derivatives

PERIODICAL: Akademiya nauk SSSR. Doklady, v. 138, no. 5, 1961, 1126-1129

TEXT: The authors studied the interaction of biscyclopentadienyl titanium $(C_2H_5)_2Ti$ with benzoyl peroxide, since the acyl peroxides are donors of acyloxy radicals and easily break the O-O bond. According to a previous paper by the authors (Ref. 1: DAN, 134, 612 (1960)), $(C_2H_5)_2Ti$ forms on thermal decomposition of biscyclopentadienyl-phenyl titanium in alcohol or benzene solution, is very reactive and sensitive to atmospheric oxygen. Benzoyl peroxide is known to destroy sandwich compounds completely (Posakker, Ref. 2: RZhKhim, 1959, No. 22, 78502). In the present case, the titanocene group was not decomposed in benzene or isopropyl alcohol in the cold by the action of benzoyl peroxide. The color of the solution changed instantaneously from dark green to dazzling yellow. CO_2 was not

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Reaction of benzoyl peroxide with...

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liberated in the reaction. The yellow crystalline product obtained in a dry nitrogen atmosphere was the expected biscyclopentadienyl titanium dibenzoate: $(C_5H_5)_2Ti(OCOC_6H_5)_2$. Since it had not yet been described, the authors also synthesized it from titanocene dichloride and silver benzoate. They checked its identity by ultimate analysis (for which T. V. Guseva is thanked), by determination of the molecular weight, the melting point, and the content of benzoate groups. $(C_5H_5)_2Ti(OCOC_6H_5)_2$ can be hydrolyzed very easily, whereby the molecule of the titanocene salt decomposes and cyclopentadiene, the salt of benzoic acid, and titanous acid are formed. On alcoholysis in absolute isopropyl alcohol, cyclopentadiene, acetone, and benzoic acid were found among the reaction products. By the action of moist air, the titanocene dibenzoate molecule loses two moles of cyclopentadiene and can be converted to dibenzoxo titanium oxide $O=Ti(OCOC_6H_5)_2$. This product is infusible. An analogous representative of compounds of the type $(C_5H_5)_2Ti(OCOR)_2$ was obtained by the reaction of titanocene dichloride with silver acetate: $(C_5H_5)_2Ti(OCOCH_3)_2$. It is yellow, melts at 127-130°C, and corresponds to biscyclopentadienyl

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25319

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B103/B220

Reaction of benzoyl peroxide with...

titanium diacetate. On alcoholysis of the latter in absolute isopropyl alcohol, acetate groups were split off and cyclopentadiene was formed to some extent. A yellow substance was precipitated, which is insoluble in organic solvents and has a structure unknown so far. Dissolved acetone was found in the isopropyl alcohol. The yellow substance mentioned was hydrolyzed completely in dilute alkali, whereby cyclopentadiene as well as acetic and titanous acids were formed. The formation of dibenzoate indicates that, unlike ferrocene, the structure of titanocene remains unchanged in this case. The authors studied the action of benzoyl peroxide on the cyclopentadienyl compounds of tetravalent titanium, i.e., on di-phenyl biscyclopentadienyl titanium. Even at room temperature, the phenyl radicals in isopropyl alcohol are replaced by the acyloxy groups of the peroxide: $(C_5H_5)_2Ti(C_6H_5)_2 + (C_6H_5COO)_2 + CH_3CH(OH)CH_3 \rightarrow (C_5H_5)_2Ti(OCOC_6H_5)_2 + 2C_6H_6 + CH_3COCH_3$. Thereby, biscyclopentadienyl titanium dibenzoate is formed. The phenyl radicals are converted into benzene by dehydration of the alcohol to acetone. The following absorption bands (in cm^{-1}) were found by comparing the infrared spectra of the final and the initial compounds: $(C_5H_5)_2Ti(C_6H_5)_2$ 448, 459, 606, 690, 720, 770, 822, 886, 930,

Card 3/4

Reaction of benzoyl peroxide with ²⁵³¹⁹

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X

1024, 1076, 1286; $(C_5H_5)_2TiCl_2$: 769, 814, 828, 872, 880, 930, 1018;
 $(C_5H_5)_2Ti(OCOCH_3)_2$: 404, 520, 600, 624, 822, 865, 1024; $(C_5H_5)_2Ti(OCOC_6H_5)_2$
720, 830, 865, 1024, 1068, 1132. The bands 822-830 and 1018-1024 cm^{-1} are
to be found in all spectra. They are interpreted by the authors as
vibrations of the cyclopentadienyl ring. The band 865 cm^{-1} is absent in
the spectra of the initial compounds, and is interpreted as belonging to
the vibrations of the Ti-O bond. There are 1 table and 3 references:
2 Soviet-bloc and 1 non-Soviet-bloc. The reference to the English-lan-
guage publication reads as follows: J. D. Varma, R. C. Mehrotra
(Ref. 3: J. Pract. Chem. 8, 64 (1959)).

ASSOCIATION: Nauchno-issledovatel'skiy institut khimii pri Gor'kovskom
gosudarstvennom universitete im. N. I. Lobachevskogo
(Scientific Research Institute of Chemistry at Gor'kiy
State University imeni N. I. Lobachevskiy)

SUBMITTED: February 20, 1961

Card 4/4

RAZUVAYEV, G.A.; SHUSHUNOV, V.A.; YABLOKOV, V.A.

Decomposition of cumene hydroperoxide catalyzed by cation
exchange resin KU-2. Dokl. AN SSSR 139 no.5:1128-1131 Ag '61.
(MIRA 14:8)

1. Nauchno-issledovatel'skiy institut khimii pri Gor'kovskom
gosudarstvennom universitete im. N.I. Lobachevskogo. 2. Chlen-
korrespondent AN SSSR (for Razuvayev).
(Cumene peroxide) (Ion exchange resins)

ETLIS, V.S.; GROBOV, L.N.; RAZUVAYEV, G.A.

Interaction of carbon sulfide with ethylene oxide. Dokl. AN SSSR
14C no.3:623-625 S '61. (MIRA 14:9)

1. Chlen-korrespondent AN SSSR (for Razuvayev).
(Carbon sulfide) (Ethylene oxide)

KHIDEKEL', M.L.; BUCHACHENKO, A.L.; RAZUVAYEV, G.A.; GORBUNOVA, L.V.;
NEYMAN, M.B.

Oxidation of β -naphthol and some of its derivatives by
peroxide compounds. Dokl. AN SSSR 140 no.5:1096-1099 0
'61. (MIRA 15:2)

1. Nauchno-issledovatel'skiy institut khimii pri Gor'kovskom
gosudarstvennom universitete im. N.I.Lobachevskogo i Institut
khimicheskoy fiziki AN SSSR. 2. Chlen-korrespondent AN SSSR
(for Razuvayev).

(Naphthol)
(Peroxides)

LEBEDEV, O.L.; KHIDEKEL', M.L.; RAZUVAYEV, G.A.

Isotopic analysis of nitrogen by the method of electron paramagnetic resonance. Dokl. AN SSSR 140 no.6:1327-1329 0 '61. (MIRA 14:11)

1. Nauchno-issledovatel'skiy institut khimii pri Gor'kovskom gosudarstvennom universitete im. N.I.Lobachevskogo i Gor'kovskiy politekhnicheskoy institut im. A.A.Zhdanova. 2. Chlen-korrespondent AN SSSR (for Razuvayev).
(Nitrogen--Isotopes) (Paramagnetic resonance and relaxation)

RAZUVAYEV, G.A.; PETUKHOV, G.G.; KAPLIN, Yu.A.; KUDRYAVTSEV, L.F.

Decomposition of diphenylmercury in cyclohexane and cyclohexene.
Dokl. AN SSSR 141 no.2:371-373 N '61. (MIRA 14:11)

1. Nauchno-issledovatel'skiy institut khimii pri Gor'kovskom
gosudarstvennom universitete im. N.I.Lobachevskogo.
(Mercury) (Cyclohexane) (Cyclohexene)

S/062/62/000/009/003/009
B179/B101

AUTHORS: Razuvayev, G. A., Grayevskiy, A. I., Minsker, K. S., and Zakharova, V. N.

TITLE: Synthesis and some properties of diethoxy aluminum peroxy cumene

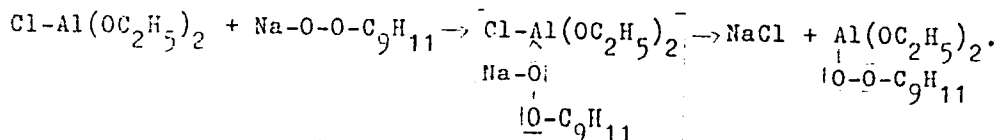
PERIODICAL: Akademiya nauk SSSR. Izvestiya. Otdeleniye khimicheskikh nauk, no. 9, 1962, 1555 - 1559

TEXT: It is sought to synthesize stable aluminum organic peroxide compounds free from impurities. Three syntheses were studied: (1) the reaction of diethoxy ethyl aluminum with cumene hydrogen peroxide, (2) that of triethoxy aluminum with cumene hydrogen peroxide, and (3) that of diethoxy aluminum chloride with the Na-salt of cumene hydrogen peroxide. Reaction (1) takes place only at temperatures higher than 15 - 20°C and in practice is not completed. Reaction (2), occurring at a maximum temperature of 28 - 30°C likewise does not complete its course and the reaction mixture contains no compound with an R-Al bond. Best results were obtained for the reaction

Card 1/3

Synthesis and some properties...

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B179/B101



This took place at 5°C in xylene solution. NaCl precipitated as fine crystals, the surplus aluminum alcoholates were evaporated and the peroxide was extracted with ether. Sometimes an amorphous complex compound having the composition $\text{AlCl(OC}_2\text{H}_5)_2 \cdot \text{NaOOC}_9\text{H}_{11}$ was precipitated with the NaCl. The peroxide $\text{C(C}_2\text{H}_5\text{O}_2\text{)AlOOC(CH}_3\text{)}_2 \cdot \text{C}_6\text{H}_5$ is a solid, white, amorphous substance which melts and decomposes at 113°C; it is easily soluble in xylene, benzene and chloroform. Its solution in xylene decomposes appreciably fast even at room temperature. At 90°C the decomposition is energetic. Its products are dimethyl-phenyl carbinol, acetophenone, α-methyl styrene, ethyl alcohol and aluminum hydroxide. The polymerization of methyl methacrylate, styrene, acrylonitrile, vinylidene chloride and vinyl chloride using $\text{(C}_2\text{H}_5\text{O)}_2\text{AlOOC(CH}_3\text{)}_2 \cdot \text{C}_6\text{H}_5$ as radical catalyst, gave a good yield of polymers. In the case of vinyl chloride, the yield of polymer

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Synthesis and some properties...

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B179/B101

increased with increasing content of peroxide in the reaction medium. The polyvinyl chloride (decomposition temperature up to 150°C, thermal stability 6 - 7 min) was amorphous and insoluble in either cyclohexanone or dichloro ethane, owing to strongly branched or net-like structure. There are 1 figure and 1 table.

ASSOCIATION: Nauchno-issledovatel'skiy institut khimii, Gor'kiy (Scientific Research Institute of Chemistry, Gor'kiy)

SUBMITTED: March 1, 1962

✓

Card 3/3

E/C62/62/000/C11/008/021
B101/B144

AUTHORS: Vyazankin, N. S., Razuvayev, G. A., and Kruglaya, O. A.
(Shchepetkova)

TITLE: Reactions of peroxides with hexaethyl distannane and hexaethyl
disilane

PERIODICAL: Akademiya nauk SSSR. Izvestiya. Otdeleniye khimicheskikh
nauk, no. 11, 1962, 2008 - 2014

TEXT: The chromatographic analysis of the products of the reaction of
hexaethyl distannane with tert-butyl peroxide at 130-135°C yielded (in
moles per mole of decomposed peroxide): 0.54 ethane, 0.87 ethylene, 0.02
methane, 0.03 butane, 0.87 tert-butanol, 0.94 triethyl-(tert-butoxy) tin,
and 0.43 of a fraction corresponding to decaethyltetrastannane by molecular
weight. Thus hexaethyl distannane reacts with tert-butyl peroxide without
cleavage of the Sn-Sn bond, which had been observed in the reaction with
acyl peroxides. A free radical mechanism according to the following reac-
tions is suggested: $(CH_3)_3COOC(CH_3)_3 \rightarrow 2(CH_3)_3CO^\cdot$; $(CH_3)_3CO^\cdot \rightarrow CH_3^\cdot$
+ CH_3COCH_3 ; $(CH_3)_3CO^\cdot + (C_2H_5)_3Sn-Sn(C_2H_5)_3 \rightarrow (C_2H_5)_3Sn-Sn(C_2H_5)_2OC(CH_3)_3$
Card 1/4

Reactions of peroxides with...

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B101/B144

+ $C_2H_5^{\cdot}$; $R^{\cdot} + (C_2H_5)_3Sn-Sn(C_2H_5)_3 \rightarrow RH + (C_2H_5)_3Sn-Sn(C_2H_5)_2C_2H_4^{\cdot}$; where

$R = (CH_3)_3CO, CH_3, \text{ or } C_2H_5$. Since equimolecular amounts of tert-butanol and triethyl-(tert-butoxy) tin were formed, disproportionation of the compound A and decomposition of the compound B are assumed, the ethylene found being also formed from compound B: $(C_2H_5)_3Sn-Sn(C_2H_5)_2C_2H_4^{\cdot}$

$\rightarrow (C_2H_5)_3Sn-Sn^{\cdot}(C_2H_5)_2 + C_2H_4$; another reaction gives decaethyl tetra-stannane: $(C_2H_5)_3Sn-Sn^{\cdot}(C_2H_5)_2 + (C_2H_5)_6Sn_2 \rightarrow (C_2H_5)_{10}Sn_4 + C_2H_5^{\cdot}$. It was found that tetraethyl tin, after irradiation with UV light, was converted to higher organo-tin compounds. These react with $AlCl_3$, with separation of metallic tin. Non-irradiated tetraethyl tin did not react with $AlCl_3$,

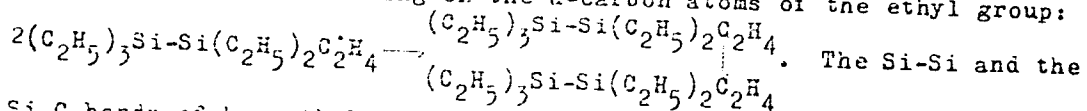
even at $150^{\circ}C$. For the homologs of hexaethyl distannane of the general formula $(C_2H_5)_3Sn-Sn(C_2H_5)_2-Sn(C_2H_5)_3$, it is assumed that, under the action of $AlCl_3$, they react similarly to hexaethyl distannane: $2(C_2H_5)_6Sn_2 \rightarrow 3(C_2H_5)_4Sn + Sn$, and decaethyl tetrastannane: $2(C_2H_5)_{10}Sn_4 \rightarrow 5(C_2H_5)_4Sn$

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Reactions of peroxides with...

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+ 3Sn. This reaction allowed the molecular weight of the higher organo-tin compounds to be estimated from the amount of released tin; and it was proven that, in the reaction of hexaethyl distannane with tert-butyl peroxide, other organo-tin compounds with higher molecular weights were formed besides decaethyl tetraastannane. The reaction of hexaethyl disilane with peroxides proceeds by a free radical mechanism, irrespective of the structure of the peroxide (benzoyl- or tert-butyl peroxide). It starts only at the decomposition temperature of the peroxide. The resulting free radicals tear hydrogen atoms away from the disilane, and the organo-silicon radicals keep on dimerizing on the α -carbon atoms of the ethyl group:



Si-C bonds of hexaethyl disilane proved stable to homolytic cleaving. There are 2 figures. The most important English-language reference is: A. B. Burg, J. R. Spielman, J. Amer. Chem. Soc., 83, 2667 (1961).

ASSOCIATION: Gor'kovskiy gosudarstvennyy universitet im. N. I. Lobachevskogo
(Gor'kiy State University imeni N. I. Lobachevskiy)

Card 3/4

Reactions of peroxides with...

S/062/62/000/011/008/021
B101/B144

SUBMITTED: April 3, 1962

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5498h
S/190/62/004/003/004/023
B110/B144

15.8061

AUTHORS: Minsker, K. S., Shapiro, I. Z., Razuvayev, G. A.

TITLE: Modification of polypropylene

PERIODICAL: Vysokomolekulyarnyye soyedineniya, v. 4, no. 3, 1962, 351-356

TEXT: The modification of polypropylene (I) was investigated by introducing functional groups into the macromolecule. The destruction of the hydroperoxides, first formed owing to the rather easy oxidation of I, was possible (1) by graft copolymerization of I with vinyl monomers polymerizing through the radical mechanism, and (2) by characteristic hydroperoxide reactions. Thereby, the number of $\begin{array}{c} | \\ -\text{C}-\text{H} \\ | \end{array}$ bonds of the unsymmetric C atom, oxidation, and aging are reduced, and ordinary dyes can be fixed at the surface of newly formed polar groups. I can be graft-copolymerized with methyl methacrylate (II), with methacryl amide, methacrylic acid, and acrylonitrile. In the last three compounds, however, the copolymers are poorly separable from the homopolymers. The graft polymer of I and II can be dyed well with azo dyes, the fiber color

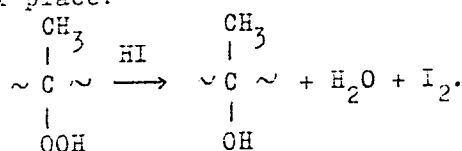
Card 1/2

Modification of polypropylene

S/190/62/004/003/004/023
B110/B144

being characterized by brilliance and resistance to boiling soapsuds. The mechanical strength (σ) was found to increase, but the relative elongation (ϵ) in the case of rupture decreased considerably due to elasticity loss. Oxidation of I only affected σ and ϵ if it was protracted (> 6 hrs) or combined with UV irradiation ($\sigma = 60 \text{ kg/mm}^2$, $\epsilon = 425 \%$; $\sigma = 79 \text{ kg/mm}^2$,

$\epsilon = 350 \%$). Only surface oxidation took place without secondary aging. The macromolecular hydroperoxide groups were identified by iodine separation. Oxidized I was treated for 6 hrs with KI acetate solution at 20°C , and the following reaction took place:



The OH groups thus formed were identified by IR spectroscopy. Here also, coloring with azo dyes was successful, and σ and ϵ increased. I fibers were made suitable for dyeing by being treated with solutions of triethyl aluminum in n-heptane and with 0.1 N HCl. The initial strength was preserved, and even partly increased. The frequency 333 cm^{-1} , identifying

Card 2/3

24985
S/190/62/004/003/005/023
B110/B144

53830

AUTHORS: Likhterov, V. R., Etlis, V. S., Razuvayev, G.A.,
Gorelik, A. V.

TITLE: Unsymmetrical organosulfonic acyl peroxides as initiators
of vinyl polymerization

PERIODICAL: Vysokomolekulyarnyye soyedineniya, v. 4, no. 3, 1962, 357-360

TEXT: Unsymmetrical organosulfonic acyl peroxides were synthesized by
interaction of the Ba salt of perbenzoic acid (from $\text{NaOCCOC}_6\text{H}_5$ and BaCl_2)
with 75 % molar excess of the corresponding sulfochloride in the presence
of an equimolecular water amount in the range 0 to 5°C:

$2\text{RSO}_2\text{Cl} + \text{Ba}(\text{OCCOC}_6\text{H}_5)_2 \xrightarrow{\text{H}_2\text{O}} 2\text{RSO}_2\text{OCCOC}_6\text{H}_5 + \text{BaCl}_2$. The following
compounds were obtained: benzoyl methane sulfonyl ($\text{CH}_3\text{SO}_2\text{OCCOC}_6\text{H}_5$) (I),
benzoyl ethane sulfonyl ($\text{C}_2\text{H}_5\text{SO}_2\text{OCCOC}_6\text{H}_5$) (II), benzoyl propane-1-sulfonyl
($\text{C}_3\text{H}_7\text{SO}_2\text{OCCOC}_6\text{H}_5$) (III), benzoyl propane-2-sulfonyl (iso- $\text{C}_3\text{H}_7\text{SO}_2\text{OCCOC}_6\text{H}_5$) (IV)

Card 1/2

Unsymmetrical organosulfonic acyl...

S/190/62/004/005/005/023
B113/B144

with yields of 43 %, 60 %, 32.7 %, 35 %, melting points 54, 46.5, 24, 49°C, active oxygen content 7.26, 6.80, 6.42, 6.35 %. Since benzoyl benzyl sulfonyl could not be separated in a pure state, the yield (28.5 %) was titrated iodometrically. Crystalline peroxides are well soluble in organic solvents except alcohols and hydrocarbons. Free from acid chloride, they can be kept for months at temperatures from -5 to 0°C. They fuse in the process of decomposition. They disengage iodine from acidulated KI solution and are decomposed by sulfochlorides. In order to determine the initiating action of II and IV (concentration: 0.004 mole/liter), the methyl methacrylate polymerization was investigated by dilatometry at different temperatures, and a considerably greater activity was established than that of benzoyl peroxide. Constants of polymerization rate at 20, 35, 45°C for II: 3.65, 17.50, 35.50 mole 0.5 liter 0.5 sec⁻¹; for IV: 4.87, 19.00, 46.20 mole 0.5 liter 0.5 sec⁻¹. Activation energy for II: 19.7; for IV: 17.5 kcal/mole. There are 1 figure, 2 tables, and 3 references: 2 Soviet-bloc and 6 non-Soviet-bloc. The two references to English-language publications read as follows: L. W. Crovatt, R.K. McKee, J. Organ. Chem., 24, 2031, 1959; I. B. Johnson, I. B. Douglass, J. Amer. Chem. Soc., 61, 2548, 1939.

SUBMITTED: February 17, 1961
Card 2/2

31908

S/190/62/004/003/008/023

B110/B144

5 3830

AUTHORS: Razuvaev, G. A., Ryabov, A. V., Zhil'tsov, S. F.,
Sokolova, V. A., Voskoboynik, G. A.

TITLE: Initiation of vinyl polymerization by organomercury compounds

PERIODICAL: Vysokomolekulyarnyye soyedineniya, v. 4, no. 3, 1962, 371-375

TEXT: On the basis of M. M. Koton's investigations (Dokl. AN SSSR, 88, 991, 1953) the effect of oxygen on the polymerization of methyl methacrylate (I) and acrylonitrile is studied at 30-50°C in the presence of dicyclohexyl mercury (II), diisopropyl mercury (III), diethyl mercury (IV) and diphenyl mercury (V), cyclohexyl mercury chloride (VI) and phenyl mercury chloride (VII). The polymerization rate increases with the temperature. The compounds do not dissociate at 30 and 50°C. II and III decompose rapidly at room temperature in the presence of small oxygen amounts. Unstable peroxide compounds which initiate the polymerization, are formed from oxygen and II and III. With stable V and mercury chlorides, oxygen has an inhibiting effect. Its increase first accelerates then decelerates polymerization owing to the decomposition of organometallic

Card 1/3

Initiation of vinyl polymerization ...

S/190/62/004/003/006/023
B110/B144

compounds and to the inhibiting effect of oxygen. Increase in oxygen pressure reduces the molecular weight to a constant value. Maximum conversion corresponds to constant minimum molecular weight and probably also to a maximum content of radicals formed. $r_1 = 0.8$, $r_2 = 0.9$ holds for

6 hrs copolymerization of styrene and I at 50°C initiated by 0.3 mole% of II, and in 14 hrs copolymerization of acrylonitrile and I at 30°C initiated by 0.3 mole% of III. Since these relative activities are similar to those of free radical copolymerization, II and III cause free radical polymerization. In the absence of O_2 , hydroquinone additions of 50-500 mole% of the initiator reduced the conversion degree of I from 12 to 2-5%, and the molecular weight from 1,500,000 to 300,000. An induction period of 5.5 hrs was found in the polymerization with IV in air. There are 3 figures and 4 tables. The most important reference to English-language publications reads as follows: F. M. Lewis, F. R. Mayo, W. F. Hulse, J. Amer. Chem. Soc., 67, 1701, 1945.

ASSOCIATION: Nauchno-issledovatel'skiy institut khimii pri Gor'kovskom gosudarstvennom universitete im. N. I. Lobachevskogo
(Scientific Chemical Research Institute of the Gor'kiy State University imeni N. I. Lobachevskiy)

Card 2/5

Initiation of vinyl polymerization ...

S/190/62/004/003/C08/C23
B110/B144

SUBMITTED: February 20, 1961

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Card 3/3

S/190/62/004/010/006/010
B101/B186

AUTHORS: Razuvayev, G. A., Minsker, K. S., Fedoseyeva, G. T.
TITLE: Heterogeneous catalytic polymerization of ethylene in the presence of $TiCl_3 + Al + AlCl_3$ or $TiCl_3 + (Al + HCl)$
PERIODICAL: Vysokomolekulyarnyye soyedineniya, v. 4, no. 10, 1962, 1495-1502

TEXT: Polyethylene (PE) and ethylene were synthesized at $60^{\circ}C$ and a pressure of 10 atm in different solvents to obtain more exact data on the polymerization of ethylene with a catalyst suggested by K. Fukui et al. (J. Polymer Sci., 37, 341, 1959; ibid., 37, 353, 1959). The system $TiCl_3 + Al + AlCl_3$ was very active, whereas its components alone or paired did not form PE. $TiCl_3 + Al$ which yields small amounts of PE, is an exception. For the first time, the activity of the catalyst was found to depend on the type of solvent (Fig. 1). The catalyst system is assumed to form a catalytically effective complex with the solvent, where $AlCl_3$ acts

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Heterogeneous catalytic polymerization ...

S/190/62/004/010/006/010
B701/B186

as activator of the Al surface and of $TiCl_3$ and forms complexes with aromatic hydrocarbons. Hence, the catalytic effect of the system $TiCl_3 + (Al + HCl)$ was tested, with Al having been treated with anhydrous HCl in an aromatic or saturated hydrocarbon medium. Treatment of Al with HCl in benzene yielded a yellowish brown $AlCl_3$ deposit which, without $TiCl_3$, was a highly active catalyst of alkylation. Benzene yielded considerable amounts of hexaethylene benzene. An addition of $TiCl_3$ caused the formation of PE. The complex thus formed, excludes structures causing alkylation of aromatics. The effectiveness of the system $TiCl_3 + (Al + HCl)$ depended on the contact time of the components before the reaction. After a contact time of 0.5 hrs, the ratio PE : hexaethyl benzene was 4 : 110, after 24 hrs 11 : 70, after 90 hrs 75 : 3, and after 120 hrs 350 : 0. $TiCl_3 + (Al + HCl)$ was more active than $TiCl_3 + Al + AlCl_3$, its presence intensified the ethylene adsorption. After an addition of $TiCl_3$, Al activated with HCl in n-heptane, did not yield PE which was only obtained

Card 2/45

Heterogeneous catalytic polymerization ...

S/190/62/004/010/006/010
B101/B186

when benzene was used for the activation, and the system was suspended in n-heptane. Both systems yielded PE with m.p. = 120 - 135°C and with physicomechanical properties consistent with those of PE produced with Ziegler catalysts. The active centers of polymerization are on the metal surface on which $TiCl_3$ is deposited. Micro- and macroformations, fibrils, spherulites, etc were observed under the polarization microscope. There are 5 figures and 3 tables.

SUBMITTED: June 10, 1961

Fig. 1: Yield of PE versus time when different solvents are used.

(1) Benzene; (2) chloro benzene; (3) toluene; (4) o-xylene; (5) cyclohexane; (6) p-dichloro benzene; (7) n-heptane.

Legend: (a) polymer yield; (b) time, hrs.

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DOMRACHEV, G.A.; RAZUVAYEV, G.A.

Interaction of dibenzenechromium (0) with acrylonitrile
and the mechanism of polymerization of the latter. Vysokom.
soed. 4 no.12:1822-1828 D '62. (MIRA 15:12)

1. Gor'kovskiy gosudarstvennyy universitet imeni
N.I. Lobachevskogo.
(Chromium compounds) (Acrylonitrile) (Polymerization)

S/190/62/004/012/009/015
B101/B186

AUTHORS: Razuvayev, G. A., Minsker, K. S., Shapiro, I. Z.
TITLE: Copolymerization of styrene and propylene in the presence
of the heterogeneous Ziegler-Natta catalytic system
PERIODICAL: Vysokomolekulyarnyye soyedineniya, v. 4, no. 12, 1962,
1833-1838

TEXT: Styrene and propylene in the initial ratio 65:35 were polymerized in the autoclave at 60°C in the presence of $TiCl_3 + Al(C_2H_5)_3$. The above-mentioned ratio was chosen in order to obtain a polymer the softening point of which is only slightly below that of isotactic polystyrene. Results: (1) The polymerization of propylene is anomalously accelerated in the presence of styrene. The initial product contains almost no styrene. Only after prolonged heating (10-15 hrs) is a copolymer obtained, which differs from the initial product and also from a mechanical mixture of the homopolymers. The thermomechanical curve for the mixture shows transition points at 160° and at 200-210°C, whereas the copolymer has a softening point only at 195-205°C. The same product is

Card 1/5

Copolymerization of styrene and...

S/190/62/004/012/009/015
B101/B196

obtained by addition of propylene in portions. This suggests that a block copolymer is formed. (2) If an aromatic hydrocarbon (benzene, xylene) is used as solvent instead of a saturated hydrocarbon (benzine, n-heptane), polymerization is accelerated. (3) The rate of polymerization also depends on the method of producing $TiCl_3$. The latter was obtained by reduction of $TiCl_4$ with H_2 , Al, Sb, or Si. The use of $TiCl_3$ obtained by reduction with H_2 or Si yielded a copolymer with s.p. 150-155°C and relative breaking elongation of 200-680%, whereas the catalyst reduced with Al or Sb yielded a copolymer with s.p. 195-208°C and relative breaking elongation 30-70%. This is explained by the difference in quality of the catalyst surface. (4) The softening point of the copolymer depends on the styrene content. In copolymers with a styrene-propylene ratio >10:1, an amorphous product is formed, the s.p. of which lies below that of polypropylene. (5) Composition and physico-mechanical properties of the copolymer can thus be regulated by the method of adding propylene, the reaction time, and the type of $TiCl_3$ used. There are 5 figures and 3 tables. The most important English-language reference is: N.G.Gaylord, H.F.Mark, Linear and Stereoregular Addition Polymers, Intersci. Publ. Inc., N.Y., 1959.

Card 2/3

Copolymerization of styrene and...

S/190/62/004/012/009/015
B101/B186

SUBMITTED: July 7, 1961

Card 3/3

38534

S/063/62/007/003/002/003
A057/A126

6.37.0

AUTHOR: Razuvaev, G.A. Corresponding Member of the Academy of Sciences of
the USSR

TITLE: Free radicals in reactions of metalorganic compounds

PERIODICAL: Zhurnal vsesoyuznogo khimicheskogo obshchestva imeni D.I. Mendeleeva,
v. 7, no. 3, 1962, 325 - 331

TEXT: Some results of investigations on free radical processes in liquids, recently carried out in the laboratories of the Gor'kovskiy universitet (Gor'kiy University), are presented and discussed. Thermo- and photo-reactions of metal-organic compounds of Li, Zn, Hg, Al, Ti, Si, Sn, Pb and others were used as sources of free radicals. Labelled compounds were used in some of the experiments. Special attention is paid to the notion of radicals in "cages" i.e. free radicals formed by dissociation of the dissolved molecule, which are surrounded by solvent molecules (thus being in a "cage"). The following investigations and their results are discussed: thermal and photo-decomposition of diphenylmercury in cyclohexane, which occurs by formation of metallic mercury and benzene. The latter is formed by the effect of phenyl radicals which split off hydrogen atoms from cyclohexane; X

Card 1/3

Free radicals....

S/063/62/007/003/002/003

A057/A126

besides, dicyclohexyl and cyclohexene is generated. These investigations were carried out by G.G. Petukhov, Yu.A. Kaplin, and A.F. Kudryavtsev. G.G. Petukhov, and S.F. Zhil'tsov studied corresponding processes in benzene as a solvent and obtained some unexpected results, which led to the assumption of complex formation between diphenylmercury and benzene. High catalytic effects of oxygen and peroxide admixtures were observed. An analogous photoreaction of tetraphenyl-lead was studied by G.G. Petukhov and Yu.A. Kaplin using labelled compounds. Because of the effect of oxygen and peroxides on the decomposition rate several corresponding experiments were carried out by the author and his co-workers with mercuryorganic compounds and are discussed. A strong effect of the nature of the solvent on the oxidation of these compounds was observed. A.V. Ryabov, S.F. Zhil'tsov, V.A. Sokolova, and G.A. Voskoboynik observed that an increased amount of oxygen inhibits the polymerization of methylmethacrylate and acrylonitril, which occurs by means of free peroxide radicals in the presence of small quantities of air in chlorine-containing solvents. N.S. Vyazankin, and O.A. Shchepetkova found that Et_2Sn polymerization can be effected also by benzoyl peroxide. The reaction of Et_2Sn with CCl_4 can be catalyzed with benzoyl peroxide at 80°C , as was observed by N.S. Vyazankin, and Yu.I. Dergunov. V.N. Latyayeva synthesized bis-cyclopentadienyl-titanium dibenzoate from $(\text{C}_2\text{H}_5)_2\text{Ti}$ in alcohol, or benzene solution in the presence

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Free radicals....

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of benzoyl peroxide. The mechanism of ethylbenzoic acid formation from Et_2Hg and acyl peroxides, investigated by Ye.V. Mitrofanova and N.S. Vyazankin, is not yet explained. The reaction of Et_6Sn_2 with acyl peroxides is assumed to occur by a hidden-radical reaction under formation of an intermediate complex, while the reaction with tert-butyl peroxide occurs in a different way than suggested by N.S. Vyazankin and O.A. Shchepetkova. Also some other reaction mechanisms with tin-organic complexes, where the formation of free radicals was observed by N.S. Vyazankin, O.S. D'yachkovskaya, O.A. Shchepetkova, and Yu.I. Dergunov are discussed in the present paper. The author concludes with the notion that results obtained with metalorganic compounds are of general importance in the studies of reaction mechanisms of other classes of organic compounds, too.

Card 3/3

X

LATYAYEVA, V. N.; MALYSHEVA, A. V.; RAZUVAYEV, G. A.

Preparation of methylmercury salts. Zhur. VKHO 7 no.5:594 '62.
(MIRA 15:10)

1. Gor'kovskiy gosudarstvennyy universitet.

(Mercury compounds)

RAZUVAYEV, G.A.; ETLIS, V.S.; GROBOV, L.N.

Interaction of some alkene oxides with carbon oxysulfide.

Zhur.ob.khim. 32 no.3:994-996 Mr '62. (MIRA 15:3)
(Ethers) (Carbonyl sulfide)

30921

S/079/62/032/003/007/007

D204/D302

11.21.41

AUTHORS: Razuvayev, G. A. and Grayevskiy, A.I.

TITLE: Synthesis of an organic peroxide of aluminum

PERIODICAL: Zhurnal obshchey khimii, v. 32, no. 3, 1962, 1006-1007

TEXT: The peroxide $\text{Al}(\text{OC}_2\text{H}_5)_2 \text{OOC}(\text{CH}_3)_2\text{C}_6\text{H}_5$ was prepared by : (1) the interaction of $\text{Al}(\text{OC}_2\text{H}_5)_2\text{Cl}$ and $\text{NaOOC}(\text{CH}_3)_2\text{C}_6\text{H}_5$, (2) the interaction of $\text{Al}(\text{OC}_2\text{H}_5)_3$ and $\text{HOOC}(\text{CH}_3)_2\text{C}_6\text{H}_5$, with and without a solvent, and (3) by the interaction of $\text{Al}(\text{OC}_2\text{H}_5)_2\text{Cl}$ with $\text{HOOC}(\text{CH}_3)_2\text{C}_6\text{H}_5$ in the presence of Na/EtOH .

In the latter case the yield was lower than in (1). The compound, a colorless powder, melted at 113°C with decomposition, was partially hydrolyzed in air and completely in acids and was extremely soluble in hydrocarbons. On heating with iso-PrOH it gave an almost quantitative yield of acetone. Like $\text{Al}(\text{OC}_2\text{H}_5)_2 \text{OOC}_2\text{H}_5$, the compound promoted the polymerization of vinyl

Card 1/2

Synthesis of an organic...

S/079/62/032/003/007/007
D204/D302

chloride and methyl methacrylate. There are 2 Soviet-bloc references.

SUBMITTED: December 13, 1961

Card 2/2

RAZUVAYEV, G.A.; LATYAYEVA, V.N.; VYSHINSKAYA, L.I.

Oxidation of bis-cyclopentadienylphenyltitanium by hydrogen peroxide.
Zhur.ob.khim. 32 no.4:1354-1355 Ap '62. (MIRA 15:4)
(Titanium compounds) (Oxidation)

ETLIS, V.S.; DEGTAREVA, L.M.; RAZUVAYEV, G.A.

Reaction of selenious anhydride with oxides of certain alkenes.
Zhur.ob.khim. 32 no.5:1508-1511 My '62. (MIRA 15:5)
(Selenium oxide) (Oxides)

RAZUVAYEV, G.A.; LIKHTEROV, V.R.; ETLIS, V.S.

Reactions of benzoylalkanesulfonyl peroxides with organic solvents.
Zhur.ob.khim. 32 no.6:2033-2039 Je '62. (MIRA 15:6)
(Sulfonic acids) (Peroxides)

RAZUVAYEV, G.A.; SHCHEPETOVA, O.A.; VYAZANKIN, N.S.

Synthesis and properties of diethyltin dibenzoate. Zhur.ob.khim.
32 no.7:2152-2154 J1 '62. (MIRA 15:7)
(Tin organic compounds) (Benzoic acid)

RAZUVAYEV, G.A.; VYAZANKIN, N.S.; GLADYSHEV, Ye.N.; BORODAVKO, I.A.

Photochemical reactions of organotin compounds with some halo
derivatives. Zhur.ob.khim. 32 no.7:2154-2160 J1 '62.
(MIRA 15:7)

(Tin organic compounds) (Halogen compounds) (Photochemistry)

RAZUVAYEV, G.A.; VYAZANKIN, N.S.; D'YACHKOVSKAYA, O.S.

Reactions of peroxide compounds with organic derivatives of silicon,
tin, and lead. Zhur.ob.khim. 32 no.7:2161-2169 J1 '62.
(MIRA 15:7)

(Peroxides) (Silicon organic compounds)
(Organometallic compounds)

RAZUVAYEV, G.A.; BOGUSLAVSKAYA, L.S.

Synthesis with free hydroxyl radicals. Part 3: Reaction of alkyl
acetates with hydroxyl radicals. Zhur.ob.khim. 32 no.7:2320-2324
Jl '62. (MIRA 15:7)
(Acetic acid) (Hydroxyl group)

RAZUVAYEV, G.A.; DERGUNOV, Yu.I.; VYAZANKIN, N.S.

Reaction of hexaethyldistannane with halo derivatives. Zhur.ob.-
khim. 32 no.8:2515-2520 Ag '62. (MIRA 15:9)
(Tin organic compounds) (Halides)

ETLIS, V.S.; GROBOV, L.N.; RAZUVAYEV, G.A.

Interaction of some alkene oxides with carbonyl sulfide. Part 2:
Zhur.ob.khim. 32 no.9:2940-2942 S '62. (MIRA 15:9)
(Ethers) (Carbonyl sulfide)

RAZUVAYEV, G.A.; MITROFANOVA, Ye.V.; KAPLIN, Yu.A.

Exchange reaction between triphenylaluminum and benzene.
Zhur.ob.khim. 32 no.10:3453 0 '62. (MIRA 15:11)
(Aluminum) (Benzene)

RAZUVAYEV, G.A.; MITROFANOVA, Ye.V.; PETUKHOV, G.G.; KAPLINA, R.V.

Oxidation of triphenylaluminum. Zhur.ob.khim. 32
no.10:3454 0 '62. (MIRA 15:11)
(Aluminum) (Radicals (Chemistry)) (Oxidation)

ETLIS, V.S.; RAZUVAYEV, G.A.

Interaction of chloro derivatives of alkenethiocarbonates
with ammonia and amines. Dokl. AN SSSR 142 no.4:838-840 F '62.
(MIRA 15:2)

1. Nauchno-issledovatel'skiy institut khimii pri Gor'kovskom
universitete im. N.I.Lobachevskogo. 2. Chlen-korrespondent
AN SSSR (for Razuvayev).

(Thiocarbonates)

(Ammonia)

(Amines)

RABINOVICH, I.B.; TEL'NOY, V.I.; KIRILLOVA, A.S.; RAZUVAYEV, G.A.

Heats of decomposition and formation of dicyclohexyl- and dimethylperoxydicarbonate. Dokl. AN SSSR 143 no.1:133-136 Mr '62. (MIRA 15:2)

1. Nauchno-issledovatel'skiy institut khimii pri Gor'kovskom gosudarstvennom universitete im. N.I.Lobachevskogo 2. Chlen-korrespondent AN SSSR (for Razuvayev).
(Peroxydicarbonic acid)

ETLIS, V.S.; RAZUVAYEV, G.A.

Interaction of 3-aminopropene-1,2-thiocarbonate with ammonia and
amines. Dokl. AN SSSR 143 no.3:633-635 Mr '62. (MIRA 15:3)

1. Nauchno-issledovatel'skiy institut khimii pri Gor'kovskom
gosudarstvennom universitete im. N.I.Lobshevskogo. 2. Chlen-
korrespondent AN SSSR (for Razuvayev).
(Thiocarbonates)(Ammonia)(Amines)

RAZUVAYEV, G.A.; MINSKER, K.S.; KRONMAN, A.G.; SANGALOV, Yu.A.; BORT, D.N.

Mechanism of homogeneous radical stereospecific polymerization
of vinyl chloride in aldehydes. Dokl. AN SSSR 143 no.5:1116-
1118 Ap '62. (MIRA 15:4)

1. Nauchno-issledovatel'skiy institut khimii pri Gor'kovskom
gosudarstvennom universitete im. N.I. Lobachevskogo. 2. Chlen-
korrespondent AN SSSR (for Razuvayev).
(Vinyl compound polymers)

VYAZANKIN, N.S.; RAZUVAYEV, G.A.; D'YACHKOVSKAYA, O.S.; SHCHEPETKOVA, O.A.

Reaction of benzoyl peroxide with triethylalkoxytin compounds.
Dokl. AN SSSR 143 no.6:1348-1350 Ap '62. (MIRA 15:4)

1. Nauchno-issledovatel'skiy institut khimii pri Gor'kovskom
gosudarstvennom universitete im. N.I.Lobachevskogo. 2. Chlen-
korrespondent AN SSSR (for Razuvayev).
(Benzoyl peroxide) (Tin organic compounds)

RAZUVAYEV, G.A.; MITROFANOVA, Ye.V.; VYAZANKIN, N.S.

Reactions of acyl peroxides with diethylmercury. Dokl. AN SSSR
144 no.1:132-134 My '62. (MIRA 15:5)

1. Nauchno-issledovatel'skiy institut khimii pri Gor'kovskom
gosudarstvennom universitet im. N.I.Lobachevskogo. 2. Chlen-
korrespondent AN SSSR (for Razuvayev).
(Peroxides) (Mercury)

RAZUVAYEV, G.A.; PETUKHOV, G.G.; ZHIL'TSOV, S.F.; KUDRYAVTSEV, L.F.

Thermal disintegration and oxidation of dicyclohexylmercury
in benzene. Dokl.AN SSSR 144 no.4:810-812 Je '62. (MIRA 15:5)

1. Nauchno-issledovatel'skiy institut khimii pri Gor'kovskom
gosudarstvennom universitete im. N.I.Lobachevskogo. 2. Chlen-
korrespondent AN SSSR (for Razuvayev).
(Mercury) (Oxidation)

S/020/62/145/002/012/018
B106/B101

AUTHORS: Razuvaev, G. A., Corresponding Member AS USSR,
Sergunov, Yu. I., and Vyazankin, N. S.

TITLE: Homolytic reactions of organotin compounds with alkyl
halides initiated by peroxides

PERIODICAL: Akademiya nauk SSSR. Doklady, v. 145, no. 2, 1962, 347-350

ABSTRACT: The reaction of small amounts of benzoyl peroxide with binary systems from an organotin compound (tetraethyl tin, dimethyl-diethyl tin, hexaethyl distannane, triethyl tin chloride) and an alkyl halide (carbon tetrachloride, n-propyl bromide) in the absence of oxygen, was studied to prove that peroxides may initiate the reaction of organotin compounds with alkyl halides. In all cases, radical chain reaction set in at 75-80°C initiated by decomposition of benzoyl peroxide. The reaction of peroxide with the system tetraethyl tin - CCl_4 , which mainly yields

triethyl tin chloride, ethylene, and chloroform, was studied in detail:
$$\text{R} \cdot + (\text{C}_2\text{H}_5)_4\text{Sn} \rightarrow \text{RH} + (\text{C}_2\text{H}_5)_3\text{Sn}\dot{\text{C}}_2\text{H}_4 \quad (\text{R} = \text{C}_6\text{H}_5\text{COO}, \text{C}_6\text{H}_5) \quad (1);$$

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B106/B101

Homolytic reactions of organotin ...

$(C_2H_5)_3Sn\dot{O}C_2H_5 \rightarrow (C_2H_5)_3Sn\cdot + C_2H_5\dot{O}C_2H_5$ (2); $(C_2H_5)_3Sn\cdot + CCl_4 \rightarrow (C_2H_5)_3SnCl + CCl_3\cdot$ (3); $CCl_3\cdot + (C_2H_5)_4Sn \rightarrow CHCl_3 + (C_2H_5)_3Sn\dot{O}C_2H_5$ etc. (4);
 or: $CCl_3\cdot + (C_2H_5)_4Sn \rightarrow CH_3CH_2CCl_3 + (C_2H_5)_3Sn\cdot$ (5). Reaction (5)
 is of minor importance as the $C_2H_5CCl_3$ yield is small. The reaction
 mixture also contains ethane and traces of butane formed by disproportiona-
 tion and dimerization of ethyl radicals which result from the reaction
 $C_6H_5COO\cdot + (C_2H_5)_4Sn \rightarrow (C_2H_5)_3SnOCOC_6H_5 + C_2H_5\cdot$ (6). Reactions (6)
 and (1) take place together. Hexachloro ethane traces form by recombination
 of $CCl_3\cdot$ radicals (chain rupture). Triethyl tin chloride may be converted
 in the same way as initial tetraethyl tin since diethyl tin dichloride
 was also isolated from the reaction mixture. This was confirmed by the
 reaction between benzoyl peroxide and the system $(C_2H_5)_3SnCl - CCl_4$.
 Peroxide caused no chain reaction with the tetramethyl tin - CCl_4 mixture.
 The reaction of hexaethyl distannane with CCl_4 initiated by peroxide was

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Homolytic reactions of organotin ...

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B106/B101

condensed and yielded great amounts of chloroform and ethylene. The ethyl groups of hexaethyl distannane are affected by the trichloroethyl radicals and triethyl tin chloride and diethyl tin dichloride are formed. The tin-tin bond in $(C_2H_5)_6Sn_2$ is ruptured; it has still to be found out whether this process is homolytic or not. Reactions (1), (2), and (3) take place when benzoyl peroxide reacts with the system triethyl tin - n-propyl bromide. Reaction (3) is completely analogous to that (with C_2H_7Br instead of CCl_4). The resulting propyl and ethyl radicals of Eq. (6) disproportionate according to the chain reaction $R^{\cdot} + (C_2H_5)_4Sn \rightarrow RH + (C_2H_5)_3Sn^{\cdot} + CH_2=CH_2$ (9); $R^{\cdot} + CH_3CH_2CH_2Br \rightarrow RH + CH_3\dot{C}HCH_2Br$ (10); $CH_3\dot{C}HCH_2Br \rightarrow CH_3-CH=CH_2 + Br^{\cdot}$ (11) ($R = C_2H_5, C_2H_7$). Studies of the decomposition of peroxide compounds in propyl bromide to confirm the courses of reactions (10) and (11) are described in a separate paper. There is 1 table.

Card 3/4

Homolytic reactions of organotin ...

S/020/62/145/002/012/018
B106/B101

ASSOCIATION: Nauchno-issledovatel'skiy institut khimii pri Gor'kovskom
gosudarstvennom universitete im. N. I. Lobachevskogo
(Scientific Research Institute of Chemistry at the Gor'kiy
State University imeni N. I. Lobachevskiy)

SUBMITTED: April 17, 1962

✓

Card 4/4

RAZUVAYEV, G.A.; KHIDEKEL', M.L.; BERLINA, V.B.

Study of the structure of organic compounds by means of electron
paramagnetic resonance. Dokl. AN SSSR 145 no.5:1071-1074 '62.
(MIRA 15:8)

1. Nauchno-issledovatel'skiy institut khimii pri Gor'kovskom
gosudarstvennom universitet im. N.I. Lobachevskogo. 2. Chlen-
korrespondent AN SSSR (for Razuvayev).
(Organic compounds) (Radicals (Chemistry)—Spectra)

S/020/62/147/002/013/021
B106/B101

AUTHORS: Gorbunova, L. V., Khidekel', M. L., Razuvayev, G. A.,
Corresponding Member AS USSR

TITLE: Free radicals in the oxidation of phenols when complex
catalysts are present

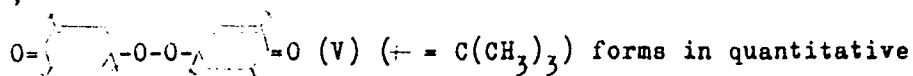
PERIODICAL: Akademiya nauk SSSR. Doklady, v. 147, no. 2, 1962, 368-371

TEXT: The oxidation of 2,4,6-tri-tert-butyl phenol (I) with oxygen was studied in the presence of "Complex A" catalyst (obtained by saturating a solution of Cu_2Cl_2 in pyridine with O_2) in order to discover whether free radicals occur and the part they play. It has been detected with the aid of e. p. r. spectra that free 2,4,6-tri-tert-butyl-phenoxy radicals (II) form in the oxidation of I. The main oxidation product is 2,6-di-tert butyl benzoquinone (III) accompanied by small amounts of 2,4,6-tri-tert-butyl-p-benzoquinol (IV). In the oxidation 0.7 mole O_2 is absorbed per mole phenol. The oxidation rate increases with increasing quantities of catalyst and reaches a constant maximum value at the molar ratio Cu_2Cl_2 :phenol = 1 : 2. The concentration of II changes with the
Card 1/3

Free radicals in the oxidation of ...

S/020/62/147/002/013/021
B106/B101

time of oxidation. With a ~40 - 50% conversion of I, the major part of the radicals disappears. Toward the end of the reaction the catalyst is completely regenerated. Addition of H_2O_2 and of acceptors for instable free radicals (benzene, methyl methacrylate) does not change the rate of O_2 absorption. When the radical II is oxidized with oxygen in the presence of "Complex A",



yield. When the amount of catalyst increases, the oxidation rate decreases. This indicates that II is stabilized when it is incorporated into the complex. These results imply that I becomes oxidized when incorporated into the catalyst complex containing 1 oxygen atom. The hydrogen of the hydroxyl group of I passes to the complex. The phenolate ion formed regenerates the catalyst and is converted to the radical II which reacts in the mesomeric p-quinoid form. The conversion of II in the complex proceeds with quinol IV as intermediary product. II as initial substance is oxidized on incorporation into a complex by the non-modified catalyst, the radical being stabilized. If a different catalyst (Complex Card 2/3

Free radicals in the oxidation of ...

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B106/B101

B" obtained by Cu_2Cl_2 oxidation in methanol) is used, the oxidation of I proceeds the catalyst participating. In this case the oxidation rate is reduced if benzene and methyl methacrylate are added. Conclusion: The direction of the oxidation of I is determined by how the catalyst is modified by the effect of the substrate. The modification is reversible and renders the process selective. This phenomenon may perhaps be one of the principles underlying the catalytic activity of ferments which ensure selectivity through a double control (by the initial catalyst and by the catalyst as modified under the effect of the reaction). There are 3 figures. ✓

ASSOCIATION: Nauchno-issledovatel'skiy institut khimii pri Gor'kovskom gosudarstvennom universitete im. N. I. Lobachevskogo
(Scientific Research Institute of Chemistry at the Gor'kiy State University imeni N. I. Lobachevskiy)

SUBMITTED: July 10, 1962

Card 3/3

S/020/62/147/003/026/027
B101/B186

AUTHORS: Razuvayev, G. A., Corresponding Member AS USSR, Minsker, K. S.,
Chernovskaya, R. P.

TITLE: Effect of organic compounds with a closed conjugated system
of π -bonds on the stereospecific polymerization of propylene

PERIODICAL: Akademiya nauk SSSR. Doklady, v. 147, no. 3, 1962, 636 - 638

TEXT: The effects of compounds containing conjugated π -bonds of benzene, diphenyl, naphthalene, and anthracene were studied on the basis of the effect of styrene on the polymerization of propylene with Ziegler catalysts as studied in previous papers (Vysokomolek. soyed., 4, no. 12, (1962)). For this purpose, the k_g/k_o ratio was determined, where k_g is the constant of propylene polymerization in the presence of the aromatic compound, and k_o is the constant of polymerization in a pure aliphatic solvent (benzine, b.p. 96 - 102°C). Polymerization was conducted at 45°C, a propylene pressure of 4.5 - 5 atm, and a catalyst concentration $C_{TiCl_3} = 0.0265 \text{ moles/l.}$

Card 1/3

Effect of organic compounds with a ...

5/020/62/147/003/026/0.7
B101/B186

Figure 1 shows that the polymerization rate is decelerated by small additions (0.3 moles/l) of aromatic compounds, and is accelerated by higher compounds. Anthracene additions could be used only up to 0.1 moles/l owing to their poor solubility in benzene. A complex with intensive donor or acceptor properties is assumed to be formed by aromatic hydrocarbon and one catalyst component. The equilibrium of this reaction depends on the structure and concentration of the additive, thus affecting the electron state of the active centers, and their ability to initiate polymerization. There is 1 figure. The most important English-language reference is: K. Vesely, J. Ambroz et al., J. Polymer Sci., 55, 25 (1961).

SUBMITTED: August 29, 1962

Card 2/3